Optical studies on the effect of pressure IV : the effects of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone

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OPTICAL STUDIES ON THE EFFECT OF PRESSURE IV

The Effects of Pressure on the Keto-Enol Equilibria of Ethyl Acetoacetate and Acetylacetone

BY JIRO OSUGI, TETUO MIZUKAMI and TADAFUMI TACHIBANA

The effects of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone in the solvents of methanol, ethanol, *iso*-propanol, *n*-hexane and *n*-heptane have been studied from the measurement of the ultraviolet spectra at high pressure.

Comparing the molal volume of the keto form with that of the enol form, which are conjectured from their parachors, it is expected that the enol form is favorable with increasing pressure.

However, the effect of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone is small. The keto-enol equilibria of ethyl acetoacetate and acetylacetone shift to the keto form in the polar solvents, and to the enol form in the non-polar solvents at high pressure.

From these results, it is expected that the variation of the dielectric constant of the solvent with pressure would have influence upon the keto-enol equilibria at high pressure. That is, it may be necessary to consider the following factors for the purpose of studying the effects of pressure on the keto-enol equilibria.

I The volume change of tautomers.

II The increment of the dielectric constant of the solvent with increasing pressure.

Introduction

As for the studies on the keto-enol equilibria, in order to determine the concentration of the enol form, the titration method[1], the molecular refraction[2], the ultraviolet spectrum[3], the infrared spectrum[4] and the nuclear magnetic resonance spectroscopy[5] have been used.

The effect of pressure on the keto-enol equilibria of ethyl acetoacetate in various solvents and the pure ester were studied by Kabachnik *et al*[6]. and Le Noble[7], respectively. However, they determined the concentration of the enol form by the titration method after releasing pressure. Kabachnik *et al.* reported that the effect of pressure varied with solvent. Some studies on the keto-enol equilibria were carried out by the ultraviolet spectrum, since Grossmann did[8].

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1) K. H. Meyer and P. Kappelmeier, *Ber.*, **44**, 2718 (1911)
2) A. Gero, *J. Org. Chem.*, **19**, 469 (1954)
3) A. S. N. Murthy, A. Balasubramanian and C. N. R. Rao, *Can. J. Chem.*, **40**, 2267 (1962)
4) R. J. W. Le Fevre and H. Welsh, *J. Chem. Soc.*, **1949**, 2230
5) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964)
6) M. I. Kabachnik, S. E. Yakushkina and N. V. Kislyakova, *Dokl. Akad. Nauk. S. S. S. R.*, **96**, 1169 (1954)
7) W. J. Le Noble, *J. Am. Chem. Soc.*, **82**, 5253 (1960)
8) P. Grossmann, *Z. physik. Chem.*, **109**, 305 (1924)

This paper reports the results obtained from the studies on the effects of pressure on the keto-enol equilibria of ethyl acetoacetate and acetylacetone in various solvents by the measurements of the ultraviolet spectra at high pressure.

Experimentals

Ethyl acetoacetate and acetylacetone, and methanol, ethanol, *iso*-propanol, *n*-hexane and *n*-heptane, commercially offered as guaranteed reagents, treated with the ordinary purification method, were used as the samples and solvents, respectively.

These solvents were chosen from the view of the following criteria.

1. No absorption band in the experimental range of wave length.
2. No solidification under the experimental pressure.
3. No reactivity with the carbonyl group.
4. No corrosive action to the optical vessel.

The optical vessel with sapphire windows is the same as reported in the previous paper[9]. The photoelectric photometer used is Hitachi EPU-2 A. The dots of spectra at the interval of 5 mμ were obtained by using these apparatuses.

In order to obtain the spectra of moderate intensity, the concentration of the solutions were 20/10000~1.6/10000 mole/*l*, owing to the path length of the optical vessel. The measurements were performed at the pressures of 1, 1000, 2000 and 3000 kg/cm^2, and at room temperature, for each solution. The optical densities of each solution at atmospheric pressure were obtained by using the ordinary quartz cell, the path length of which was 1.0 cm.

Results and Discussion

The position and the intensity of the absorption band: The positions and the intensities of absorption maxima of ethyl acetoacetate and acetylacetone in each solvent were investigated at atmospheric pressure, which are due to the enone structure, *i. e.*

—C(OH)=C—CO—

The results are shown in Figs. 1 and 2, respectively. Figs. 1 and 2 show that the effect of solvent on the keto-enol equilibria of ethyl acetoacetate and acetylacetone at atmospheric pressure, respectively. That is, the keto-enol equilibria of these substances shift to the enol form with decreasing polarity of the solvent.

Determination of the concentration of the enol form by the spectra: The absorption band of the enol form overlaps with that of the keto form in the region of 240~275 mμ. However, the determination of the concentration of the enol form in the given solvent is performed by using the following equation,

9) J. Osugi and Y. Kitamura, *This Journal*, 35, 25 (1965)

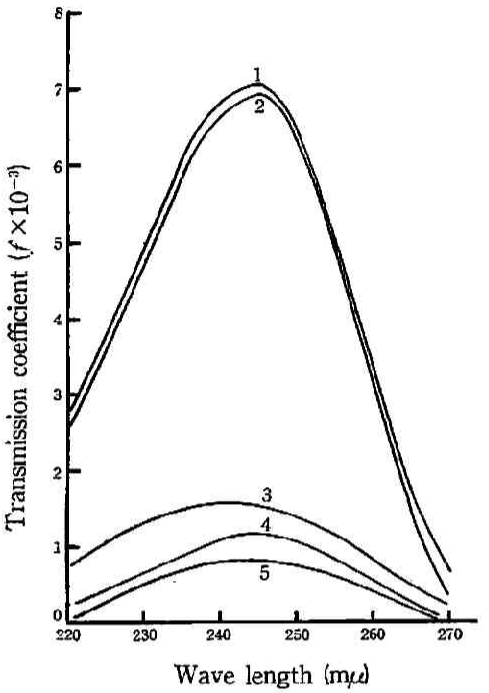


Fig. 1 The ultraviolet spectra of ethyl acetoacetate in the solvent of 1) *n*-heptane, 2) *n*-hexane, 3) *iso*-propanol, 4) ethanol and 5) methanol

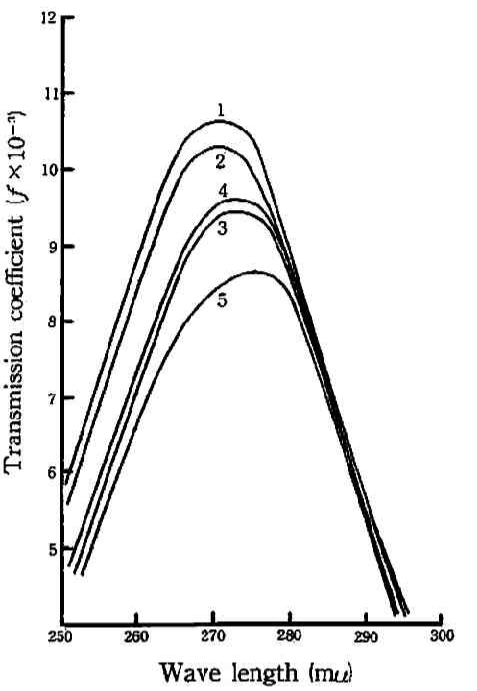


Fig. 2 The ultraviolet spectra of acetylacetone in the solvent of 1) *n*-heptane, 2) *n*-hexane, 3) *iso*-propanol, 4) ethanol and 5) methanol

$$f=f'\frac{E}{100}+f''\frac{100-E}{100}, \tag{1}$$

where E is the percent concentration of the enol form, f is the apparent extinction coefficient, f' and f'' are the molal extinction coefficients of the enol form and the keto form, respectively. In general, f' is much larger than f'' so that f'' is negligible as compared with f'. Then,

$$f=f'\frac{E}{100}. \tag{2}$$

Knowing the values of f and E, the value of f' can be calculated by equation (2). On the other hand, for each solution,

$$\frac{f_p}{f}=\frac{E_p}{E}, \tag{3}$$

where f and E are the apparent extinction coefficient and the concentration of the enol form at atmospheric pressure, respectively, f_p and E_p are those of the enol form at the pressure of P. f_p is corrected for the change of the concentration due to compression. By equation (3), the concentration of the enol form at high pressure can be calculated. For this purpose, the assumption is made. That is, the extinction coefficients do not vary with pressure. Therefore, the change of the apparent extinction coefficient with pressure is due to the change of the keto-enol equilibrium.

f' of ethyl acetoacetate and acetylacetone are calculated by equation (2) using the values of E[1)3)13)] in the solvents of methanol, ethanol and *n*-hexane. The average values of f' are 14500 and 1200 for ethyl acetoacetate and acetylacetone, respectively.

Table 1 Concentration of enol form (at atmospheric pressure)

Solvent	Ethyl acetoacetate	Acetylacetone
methanol	5.7%	72.0%
ethanol	8.8	80.0
iso-propanol	10.8	79.2
n-hexane	48.0	85.9
n-heptane	48.8	89.1

Time required to reach at equilibrium after compression: The time required to reach at equilibrium after compression is examined. There is no difference between the spectrum immediately after compression and that after 18 hours. This means that the system is allowed to reach at equilibrium immediately after compression, so that the measurements of the spectra are carried out immediately after compression.

At atmospheric pressure, it was reported in some papers[6)~8)] that the time required to reach at equilibrium after preparing the solution was long, but the concentration of the solution was relatively high. On the other hand, in this experiment, the dilute solutions were used so that the time required to reach at equilibrium after compression might be short.

Effect of pressure on the keto-enol equilibria: The extinction coefficients in the range of 240~275 mμ of ethyl acetoacetate and acetylacetone in the solvents of methanol, ethanol, *iso*-propanol, *n*-hexane and *n*-heptane were measured at the pressures of 1, 1000, 2000 and 3000 kg/cm². The result

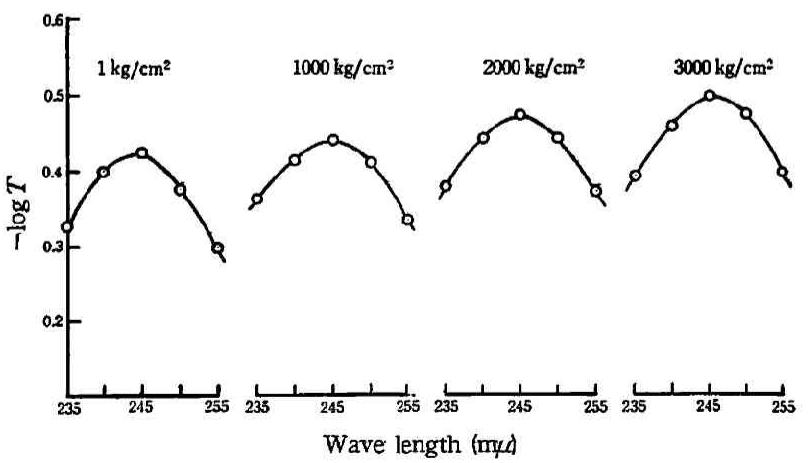


Fig. 3 The ultraviolet spectra of ethyl acetoacetate in the solvent of *n*-hexane at high pressure

obtained for ethyl acetoacetate in *n*-hexane is shown in Fig. 3 as an example.

In order to determine the concentration of the enol form in each solvent at high pressure, the correction for the change of the concentration due to compression must be done. The concentration at high pressure is shown by the following equation,

$$C^p=\frac{m}{AS+Bs_m}\simeq\frac{m}{AS}\ , \qquad (4)$$

where m is the number of moles of solute, S and s_m are the volumes of solvent and solute, respectively, A and B are the relative molal volumes in terms of the volumes at atmospheric pressure, of the slovent and the solute, respectively. s_m is negligible as compared with S, for the solutions are very dilute, so that equation (4) is reduced. The relative volumes[10] of the solvents are shown in Table 2. f_p in each solvent at high pressure is shown in Table. 3.

Table 2 Relative volume at 20°C (V_p/V_1)

Pressure (kg/cm²)	methanol	ethanol	*iso*-propanol	*n*-hexane	*n*-heptane
1	1.000	1.000	1.000	1.000	1.000
1000	0.931	0.931	0.932	0.909	0.914
2000	0.888	0.889	0.895	0.864	0.871
3000	0.859	0.860	0.868	0.834	0.841

Table 3 f_p

Solvent \ Pressure (kg/cm²)	Ethyl acetoacetate				Acetylacetone			
	1	1000	2000	3000	1	1000	2000	3000
methanol	820	740	670	640	8640	7740	7590	8000
ethanol	1280	1210	1130	1090	9600	9590	9120	9400
iso-propanol	1560	1520	1580	1640	9500	8950	9950	10270
n-hexane	6960	7000	7080	7190	10300	9850	9800	10350
n-heptane	7080	7160	7200	7260	10700	10390	10820	10820

Table 4 Keto-enol equilibrium constant

Solvent \ Pressure (kg/cm²)	Ethyl acetoacetate				Acetylacetone			
	1	1000	2000	3000	1	1000	2000	3000
methanol	0.060	0.054	0.048	0.038	2.57	1.82	1.72	1.99
ethanol	0.096	0.087	0.085	0.081	4.00	3.98	3.17	3.63
iso-propanol	0.121	0.117	0.122	0.127	3.81	3.90	4.85	5.90
n-hexane	0.923	0.934	0.953	0.984	6.09	4.56	4.46	6.25
n-heptane	0.953	0.976	0.984	0.996	8.17	6.52	8.35	8.35

10) P. W. Bridgman "The physics of high pressure", p. 128, G. Bell and Sons, Ltd., London (1958)

The concentrations of the enol form in each solvent at high pressure were calculated by equation (3) using the values of f_p. Then, the keto-enol equilibrium constants were also calculated. The results are shown in Table 4 and Figs. 4 and 5 as the keto-enol equilibrium constants.

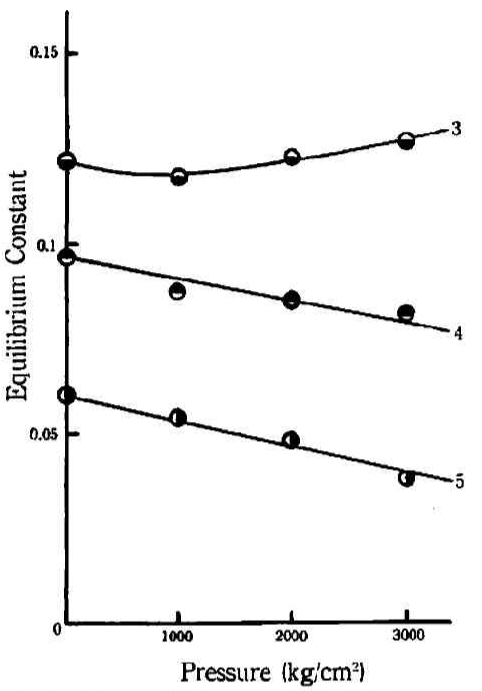


Fig. 4 The equilibrium constant of tautomerism for ethyl acetoacetate at high pressure (code number refer to solvents of Fig. 1)

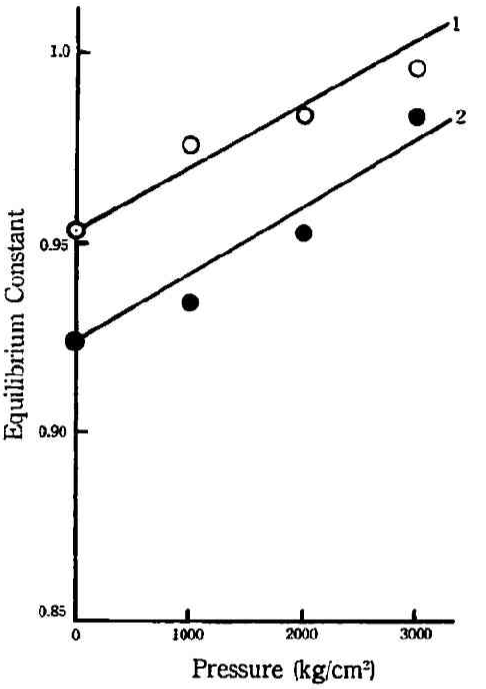
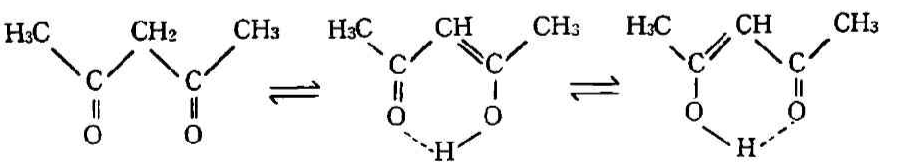


Fig. 5 The equilibrium constant of tautomerism for ethyl acetoacetate at high pressure (code number refer to solvents of Fig. 1)

The keto and enol tautomers of ethyl acetoacetate and acetylacetone are shown in equations (5) and (6), respectively.

(5)



(6)

The parachors[11] and the molal volumes of ethyl acetoacetate and acetylacetone were calculated. The parachors were calculated from their atomic structure and then the molal volumes were estimated.

11) O. R. Quayle, *Chem. Rev.*, **53**, 439 (1953)

The parachor is represented by equation (7),

$$P=\frac{M\gamma^{1/4}}{D-d}, \tag{7}$$

where M is the molecular weight, D and d are the densities of the liquid phase and the gas phase, respectively, and γ is the surface tension. In equation (7), d being negligible as compared with D and assuming to be $\gamma_k \simeq \gamma_e$, then equation (8) is reduced,

$$P_e \cdot D_e \simeq P_k \cdot D_k, \tag{8}$$

where suffixes e and k represent the enol form and the keto form, respectively.

Assuming that the density of ethyl acetoacetate in the liquid phase is equal to that of the keto form of ethylacetoacetate, because the keto form is predominant in ethyl acetoacetate, by equation (8), the density of the enol form of ethyl acetoacetate is calculated. Then, the molal volume of the enol form of ethyl acetoacetate is estimated. On the other hand, assuming that the density of acetylacetone in the liquid phase is eqaul to that of the enol form of acetylacetone, because the enol form is predominant in acetylacetone, by equation (8), the density of the keto form of acetylacetone are calculated. Then, the molal volume of the keto form of acetylacetone is estimated. The results are shown in Table 5. That is, the molal volumes of the enol forms of ethyl acetoacetate and acetylacetone are smaller than those of the keto forms, by 11.0~13.8 ml/mole, respectively.

Table 5 Parachor and calculated molal volume

		Parachor	Molal volume (ml/mole)
Ethyl acetoacetate	keto form	303.3	126.5
	enol form	277.0	115.5
Acetylacetone	keto form	246.0	116.4
	enol form	218.8	102.6

The difference of volume between the keto form and the enol form, ($\Delta V = V_e - V_k$) which is estimated by equation (9), is very small in absolute value, and even positive.

$$\Delta V = -\frac{RT}{P_{\mathrm{I}} - P_{\mathrm{II}}} \log \frac{K_{\mathrm{I}}}{K_{\mathrm{II}}} \tag{9}$$

In general, the keto-enol equilibria shift to the keto form in the polar solvent, and to the enol form in the non-polar solvent, respectively. According to Powling *et al*[12]., there is a linearity between the free energy change (ΔG) for the keto-enol equilibria of ethyl acetoacetate and acetylacetone, and the dielectric property, $\{(\varepsilon-1)/(2\varepsilon+1)\}\rho/M$, where ε, ρ and M are the dielectric constant, the density and molecular weight, respectively.

According to thermodynamics

12) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, 73, 4353 (1951)

$$\ln K = -\frac{\Delta G}{RT}, \tag{10}$$

$$K = \frac{[\text{Enol}]}{[\text{Keto}]}.$$

Then, it is expected that there is a linearity between $\log K$ and $\{(\varepsilon-1)/(2\varepsilon+1)\}\ \rho/M$. Plotting $\log K$[1)3)13)] against$\{(\varepsilon-1)/(2\varepsilon+1)\}\rho/M$, the results are obtained as shown in Figs. 6 and 7. That is, the keto-enol equilibrium constants decrease with increasing the dielectric constants of the solvents.

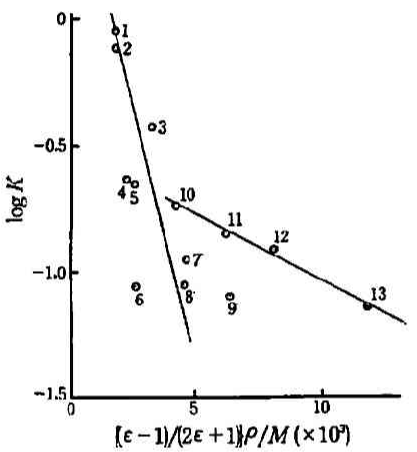


Fig. 6 Equilibrium constant of tautomerism for ethyl acetoacetate *vs.* solvent property $\{(\varepsilon-1)/(2\varepsilon+1)\}\rho/M$

1) hexane
2) cyclohexane
3) ether
4) toluene
5) benzene
6) dioxane
7) nitrobenzene
8) chloroform
9) acetone
10) amylalcohol
11) propanol
12) ethanol
13) methanol

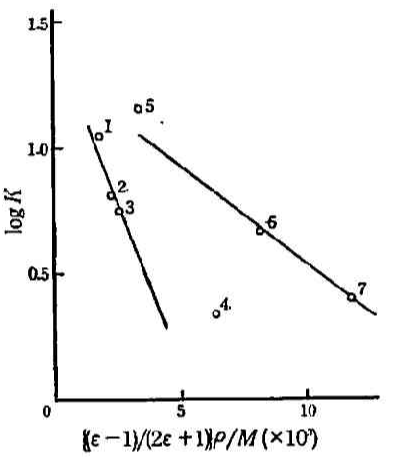


Fig. 7 Equilibrium constant of tautomerism for acetylacetone *vs.* solvent property $\{(\varepsilon-1)/(2\varepsilon+1)\}\rho/M$

1) hexane
2) toluene
3) benzene
4) acetone
5) ether
6) ethanol
7) methanol

Plotting the dielectric constants against pressure[14)], the results are obtained as shown in Fig. 8. That is, the dielectric constants of the solvents increase with pressure. This view is confirmed by the fact that the absorption spectra show the red shift at high pressure. Assuming that the results as shown in Figs. 6 and 7 hold at high pressure, the keto-enol equilibrium constants decrease with increasing pressure.

13) K. H. Meyer, *Ber.*, **44**, 2725 (1911), **45**, 2843 (1912), **47**, 826 (1914)
J. B. Conant and A. F. Thompson, *J. Am. Chem. Soc.*, **54**, 4039 (1932)

14) W. E. Danforth, *Phys. Rev.*, **38**, 1224 (1931)
S. Kyropoulos, *Z. Physik.*, **40**, 507 (1927)
C. Francke, *Ann. Physik.*, **77**, 159 (1925)

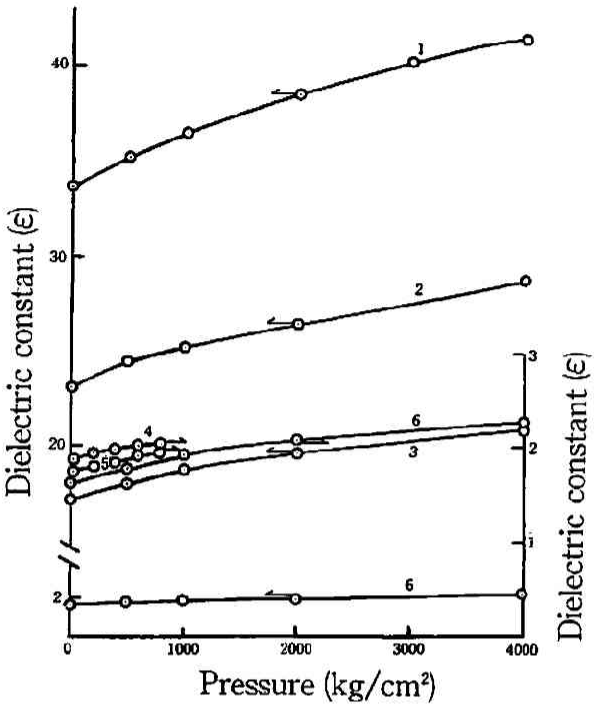


Fig. 8 Dielectric constant at high pressure
1) methanol 4) heptane
2) ethanol 5) hexane
3) *iso*-butanol 6) pentane

The effects of pressure on the keto-enol equilibrium constant can be divided into two parts.

I The volume change of tautomers.

II The increment of the dielectric constant of the solvent with increasing pressure.

These effects is considered to oppose each other. In the solvents of *n*-hexane and *n*-heptane, the increments of the dielectric constants with pressure are small, so that the first effect is preferable. Therefore the keto-enol equilibria shift to the enol form with pressure. In the solvents of methanol and ethanol, the increments of the dielectric constants with pressure are large, so that the second effect is preferable. Therefore, the keto-enol equilibria shift to keto form with pressure. In the solvent of *iso*-propanol, the increment of the dielectric constant with pressure is small, so that the keto-enol equilibrium shifts to the enol form at sufficiently high pressure.

The same consideration is adaptable to the effect of pressure on the keto-enol equilibrium of acetylacetone. However, the increment of the equilibrium constant is small. This may be due to the large equilibrium constant even at atmospheric pressure. According to these considerations, the ΔV for ethyl acetoacetate, is 8~10 ml/mole, which seems to be in agreement with the results of parachors.

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